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Scope of Research

Depletion of fossil and rare metal resources, which the chemical industry relies on, is crucial problem for human society. Our research activity is devoted to the discovery, design and development of new molecular transformation reactions that enable efficient exploitation of chemical resources, such as unsaturated hydrocarbons, haloalkanes, etc. The present research subjects are (1) a substitution reaction of unreactive haloalkanes with various organometallic compounds promoted by feedstock metals such as iron, zinc, and magnesium (2) understanding and design of synergetic effects of multi-metallic centers on the catalysis by the use of quantum chemistry.

Research Activities (Year 2006)

Presentations

Development of New Organometallic Substitution Reactions toward Exploitation of Chemical Resources, Nakamura M, 1st European Chemistry Congress, Budapest, Hungary, 27–31 August 2006.

Iron-Catalyzed Cross Coupling of Haloalkanes, Ito S, Nakamura M, 1st International Conference on Cutting-Edge Organic Chemistry in Asia Tiruru, Naha, Okinawa, Japan, 16–20 October 2006.

Cross Coupling of Haloalkanes under Iron Catalysis, Nakamura M, 98th Catalysis Society of Japan Meeting, Toyama, Japan, 26–29 September 2006.

Grants

Nakamura M, Development of Iron Catalyzed Reaction for Transformation of Polyvinylchloride, Grant-in-Aid for Exploratory Research, 1 April 2005–31 March 2007.

Nakamura M, Molecular Transformation of Unreactive Haloalkanes, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2006–31 March 2007.

Nakamura M, Design and Application for Methodology of Multi-Metallic, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2006–31 March 2010.

Hatakeyama T, Development of SN2 Reaction of Carbon-Heteroatom Bond with Highly Reactive Metal Enolate, Grant-in-Aid for Young Scientists (Start), 1 April 2006–31 March 2008.

Awards

Nakamura M, Lectureship Award to China, 1st International Conference on Cutting-Edge Organic Chemistry in Asia, 20 October 2006.

Nakamura M, Lectureship Award to Hong Kong, 1st International Conference on Cutting-Edge Organic Chemistry in Asia, 20 October 2006.

Nakamura M, Banyu Young Chemist Award 2006, Banyu Life Science Foundation International, 18 November 2006.

Hatakeyama T, Kaneka Award in Synthetic Organic Chemistry, The Society of Synthetic Organic Chemistry, Japan, 30 November 2006.

Iron Catalyzed Cross-Coupling Reaction

Chloroalkanes, derived from olefins in one step, are feedstock carbon resources in industry. However, there are few methods to transform C–Cl bond into C–C bond directly under mild conditions due to its chemical stability. We have developed several iron-catalyzed C–C bond formation reactions, enantioselective olefin carbometalation reaction and diastereoselective addition/ring-opening reaction. Recently, we found cross-coupling reaction of haloalkanes and aryl magnesium compounds takes place in the presence of $FeCl_3$ and *N, N, N', N'*-tetramethylethylenediamine (TMEDA). Under these conditions, even secondary alkyl chlorides, known to be unreactive substrate for substitution reaction, gave coupling products in up to 99% yield. The use of aryl zinc compounds, which shows mild nucleophilicity and basicity, enable to introduce functional groups such as ester and nitrile on the alkyl and/or aryl moieties.

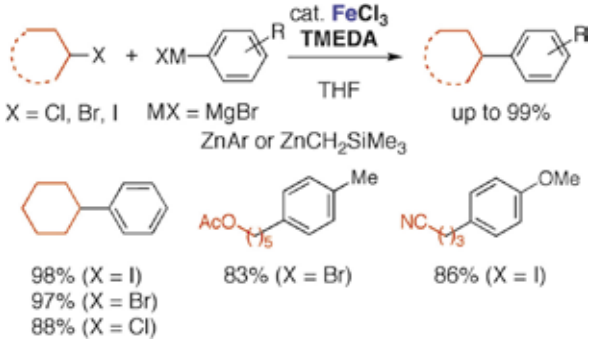

Figure 1. Iron-Catalyzed Cross-Coupling Reaction.

The liquid crystal (LC) molecules used for active matrices LC displays, such as TV, PC, and portable phones, widely have a fluoroarylcyclohexane substructure as a mesogen moiety. As shown in Figure 1, iron catalyzed cross-coupling reaction of functionalized aryl zinc compounds and chlorocyclohexanes (or bromocyclohexanes) can construct the phenylcyclohexane skeleton in shorter steps from cheaper starting materials than the present industrial methods (9 steps), which consume expensive and toxic transition metal catalysts, such as palladium and nickel.

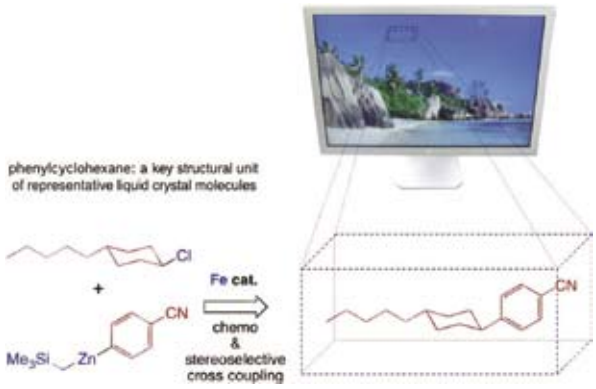

Figure 2. Facile synthesis of liquid crystal molecules.

SN2 Reaction of Haloalkanes with Magnesium Enamides

SN2-type substitution reaction at asymmetric carbon center, yielding Walden inversion product, is known to be a powerful tool in controlled organic synthesis. However, it is difficult to carry out SN2 reaction with carbon nucleophiles due to its sterical hindrance and considerable basicity. Recently, we found that magnesium enamide, possessing chelate structure, is highly nucleophilic and moderately basic to substitute secondary haloalkanes. It is noteworthy that unreactive haloalkanes, fluro- and chloroalkanes smoothly react with magnesium enamide to provide α-alkylated ketones in up to 97% yield upon hydrolysis of imine moiety and optically active chloroalkanes give the corresponding "Walden inversion" adduct with high enantioselectivity.

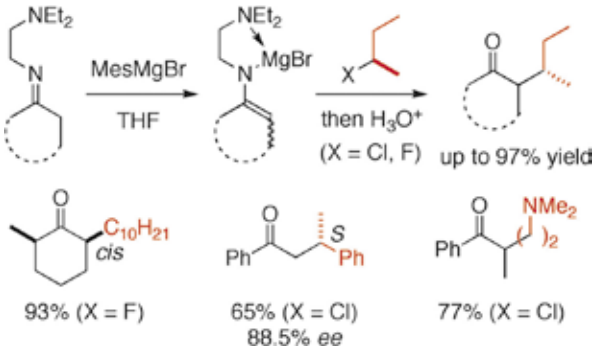

Figure 3. SN2 Substitution Reaction of Fluoro- and Chloroalkanes.